

VERNIKOVSKIY, K.B.; LUBENETS, I.P.; ORLOV, V.S.; SHCHELKANOV, V.A.;
DENISOV, Ye.M.

Induced block caving at the Gora Blagodat' mine. Gor. zhur.
no. 12:29-32 D '65. (MIRA 18:12)

1. Goroblagodat'skaya zhelezorudnoye mestorozhdeniye (for
Vernikovskiy, Lubenets, Orlov). 2. Institut gornogo dela,
Sverdlovsk (for Shchelkanov, Denisov).

DENISOV, Ye.N.; MATVEYENKO, Ye.G.

Purification of radioiodine-labeled Rose Bengal from admixtures of unbound radioiodine. Med. rad. 10 no.11:65-66 N '65.

(MIRA 19:1)

1. Laboratoriya radioisotopnoy diagnostiki (zav. - prof. M.N. Fateyeva) Instituta meditsinskoy radiologii AMN SSSR. Submitted December 12, 1963.

L 3707L-66 EWT(1)/T JK

ACC NR: AP6013759

(A)

SOURCE CODE: UR/0241/65/010/011/0065/0066

AUTHORS: Denisov, Ye. N.; Matveyenko, Ye. G.

27
B

ORG: Institute of Medicinal Radiology, AMN SSSR, Laboratory of Radioisotopic Diagnostics, Professor M. N. Fateyeva, Director (Institut meditsinskoy radiologii AMN SSSR, Laboratoriya radioizotopnoy diagnostiki)

TITLE: Removal of free I^{131} from I^{131} -labelled Bengal rose

SOURCE: Meditsinskaya radiologiya, v. 10, no. 11, 1965, 65-66

TOPIC TAGS: radiation chemistry, chemical labelling, diagnostic medicine, *anionite*, iodinated organic compound, ion exchange chromatography / AV-17 anionite

ABSTRACT: A method for the removal of free I^{131} ⁶contaminating industrially prepared I^{131} -labelled Bengal rose is described. The procedure is of importance because the presence of free I^{131} distorts the diagnostic data obtained by using I^{131} -labelled Bengal rose in liver diseases. The method consists of passing Bengal rose in glycine buffer solution through an ion exchange column filled with anionite AV-17 (in Cl^- form) at a rate of 0.5--1 ml/min. The amount of free I^{131} in the

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UDC: 616-073.916:615.42

L 37074-66

ACC NR: AP6013759

technical preparation was reduced from 9.28 to 0.35%. The purified preparation was considerably more stable to sterilization by boiling. Orig. art. has: 1 figure and 1 table.

SUB CODE: 07, 06/ SUBM DATE: 12Dec63

no
Card 2/2

S/181/63/005/004/026/047
B102/B186

AUTHORS: Shohemelev, V. N., Rumsh, M. A., and Denisov, Ye. P.

TITLE: Determination of thickness and efficiency of the yield zone of true secondary electron emission based on an investigation of the energy spectrum of X-ray photoemission

PERIODICAL: Fizika tverdogo tela, v. 5, no. 4, 1963, 1132 - 1137

TEXT: The X-ray photoemission energy spectrum of NaCl, KCl and KBr photocathodes, condensed in vacuo onto Al or Au substrata, were analyzed in order to determine the thickness of the yield zone l and its efficiency $S = \nu - 1$, where ν is the mean number of electrons contained in the wave packet (cf. FTT, 4, 2795, 1962), $\nu = I/I_x$, I being the total current in the case of zero delay, and I_x the current due to X-ray photoelectrons. The layer thicknesses investigated were between several tens and several thousands of Å about ten different cathodes were measured for each pair substratum-salt, placed in a spherical capacitor. The electrometer used had a sensitivity of 10^{-14} A so that $\nu = I/I_x$ obtained from the volt-ampere characteristics was

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Determination of thickness and...

S/181/63/005/004/026/047
B102/B186

very accurate. The results were found to be affected by an additional mechanism of emission which had to be taken into account when determining S. The current due to this mechanism was calculated using the relation

$i_{add} = \frac{\kappa_1 - \kappa_r}{\kappa_r} i_r$, where κ_1 is the quantum yield determined by the ratio number of emission events/ number of absorbed quanta; κ_r is the X-ray quantum yield, the ratio number of X-ray electrons emitted into vacuum/number of quanta. For metals $\kappa_1 = \kappa_r$, but for dielectrics $\kappa_1 > \kappa_r$. The additional mechanism most probably becomes apparent only when besides irradiation also an electric field acts on the cathode; in the present case this field was ~ 1 kv/cm. The following results were obtained:

	l	v	S	S'	
NaCl	1000 \pm 100 Å	22	21	18	$S = (I - i_r)/i_r$
KCl	600 \pm 100 Å	18	17	15	$S' = (I - i_{add} - i_r)/i_r$
KBr	500 \pm 100 Å	24	23	21	

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Determination of thickness and...

S/181/63/005/004/026/047
B102/B186

Only if the salt layer thickness is smaller than the Debye radius, S depends on the substratum properties. There are 5 figures and 1 table.

ASSOCIATION: Leningradskiy gosudarstvennyy universitet (Leningrad State University)

SUBMITTED: November 21, 1962

Card 3/3

L 12645-65 EWA(k)/EWP(1)/EPA(s)-2/EWG(k)/EWT(m)/T/EEC(t)/EPR/EWP(b) Pz-6/
Ps-4/Pt-10 IJP(c) ID/JC/AT

ACCESSION NR: AP4044922

S/0181/64/006/009/2569/2573

AUTHORS: Denisov, Ye. P.; Shchemelev, V. N.; Mezhevich, A. N.;
Rumsh, M. A.

TITLE: Analysis of the energy composition of x-ray photoemission
from a bulky cathode

SOURCE: Fizika tverdogo tela, v. 6, no. 9, 1964, 2569-2573

TOPIC TAGS: x ray emission, x ray spectrum, photoemission, cathode,
K band, L band

ABSTRACT: The purpose of the investigation was to separate the
parts connected with the K, L, Auger, and secondary electrons from
the total photoemission, and to compare the relative number of elec-
trons in each group with the corresponding coefficients in the formu-
la for the quantum yield. To this end, the method of spherical
capacitor was used to study the energy composition of the x-ray pho-

Card 1/2

L 12645-65

ACCESSION NR: AP4044922

toemission for aluminum, chromium, titanium, and iron photocathodes. The setup used was described by two of the authors (Rumsh and Shchemelev, FTT v. 5, 71, 1963). A graphic procedure for separating the various components is described. The results confirm the validity of the equation derived previously by the Rumsh and Shchemelev (ZhETF v. 42, 727, 1962) for the quantum yield of the external photoeffect. "The authors thank Academician A. A. Lebedev for interest in the work and for a discussion of the results." Orig. art. has: 3 figures, 1 formula, and 1 table.

ASSOCIATION: Leningradskiy gosudarstvennyy universitet (Leningrad State University)

SUBMITTED: 28Nov63

ENCL: 00

SUB CODE: OP, SS

NR REF SOV: 008

OTHER: 000

Card 2/2

L 12610-65 EWA(k)/EWT(1)/EWI(k)/EWT(n)/EPA(sp)-2/EPT(n)-2/EPA(w)-2/
EEC(t)/T/EWP(t)/EWA/EWP(b) Pz-/Pab-10/Pz-1 IJP(c) AT/EWH/JD

ACCESSION NR: AP4044923

B/0181/64/006/009/2574/2579

AUTHORS: Shchemelev, V. N.; Yelisyenko, L. G.; Denisov, Ye. P.;
Rumsh, M. A.

TITLE: Current and pulse measurements of x-ray photoemission of a bulky cathode

SOURCE: Fizika tverdogo tela, v. 6, no. 9, 1964, 2574-2579

TOPIC TAGS: x ray emission, photoemission, cathode, metallic photocathode, dielectric photocathode, electron multiplier, secondary electron multiplier

ABSTRACT: It is shown, after reviewing the earlier literature and the various measurement methods, that the discrepancies in the results obtained from metals and dielectrics are due to certain peculiarities in emission from these substances. Metallic photocathodes are characterized by emission of fast x-ray electrons unaccompanied

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I 12640-65

ACCESSION NR: AP4044923

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by slow truly secondary satellites, so that measurement of emission with the aid of secondary-electron multipliers of the open type fails to record an appreciable part of this emission. In the case of dielectric photocathodes, an appreciable fraction of the emission acts consists of purely secondary events, the number of which increases as the thicknesses for the yield of x-ray and secondary electrons become equalized and as the secondary emissivity of the dielectric medium increases. It is therefore possible to explain the discrepancy between the number of x-ray electrons emitted into vacuum from a dielectric and the number of produced x-ray electrons in dielectrics without resorting to an additional emission mechanism. Experimental data are presented for the average number of electrons per emission act. The corresponding emission coefficients and frequencies of emission acts are tabulated for various dielectrics (NaCl, KCl, KBr, CsCl, CsI) and metals (Al, Ti, Cr, Fe, Co, Sn, Au, Pb, and Bi). The effect of coating metals with dielectrics is also briefly discussed. "The authors thank Academician A. A. Lebedev for

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L 12640-65

ACCESSION NR: AP4044923

interest in the work and for a discussion of the results." Orig.
art. has: 2 formulas and 3 tables.

ASSOCIATION: Leningradskiy gosudarstvennyy universitet (Leningrad
State University)

SUBMITTED: 28Nov63

ENCL: 00

SUB CODE: SS, OP

NR REP SOV: 007

OTHER: 000

Card 3/3

SHCHEMELEV, V.N.; YELISEYENKO, L.G.; DENISOV, Ye.P.; RUMSH, M.A.

Current and pulse measurements of the X-ray photoemission from
a massive cathode. Fiz. tver. tela 6 no.9:2574-2579 S '64.
(MIRA 17:11)

1. Leningradskiy gosudarstvennyy universitet.

DEKISOV, Ye.P.

Formation of the low-lying shores of the southern Maritime Territory.
Soob.DVFAK SSSR no.10:246-248 '59. (MIRA 13:11)

1. Dal'nevostochnyy filial Sibirskogo otdeleniya AN SSSR.
(Maritime Territory--Shore lines)

DENISOV, Ye.P.

Stratigraphy of upper Cenozoic formations of the southwestern Maritime Territory. Soob.DVFAK SSSR no.12:19-23 '60. (MIRA 13:11)

1. Dal'nevostochnyy filial imeni V.L.Komarova Sibirskogo otdeleniya AN SSSR.

(Maritime Territory—Geology, Stratigraphic)

DENISOV, Ye.P.

New data on the basalts of the Maritime Territory. Geol. i geofiz.
no.12:48-56 '60. (MIRA 14:5)

1. Del'nevostochnyy filial Sibirskogo otdeleniya AN SSSR, Vladivostok.
(Maritime Territory--Basalt)

S/519/60/000/008/023/031
D051/D113

AUTHORS: Denisov, Ye. P.; Smirnov, A. M.

TITLE: On the latest tectonic movements of the southern coastal region of the Primorskiy kray and adjacent territories

SOURCE: Akademiya nauk SSSR. Sovet po seysmologii. Byulleten', no. 8, Moscow, 1960. Voprosy seysmicheskogo rayonirovaniya, 179-183

TEXT: A brief survey of the geologic-tectonic development of the southern coastal region of the Primorskiy kray and adjacent territories is given. Continental conditions were established as a result of folding and uplifts in areas which were inundated by the sea before the end of the Cretaceous period. A number of depressions and axially oriented elevations formed during the Paleogene, but the main characteristic, however, was planation. The correlation between depressions and elevated zones did not remain constant and some depressions rose to different heights, even up to 600 m, a process due to increased tectonic activity at the end of the Miocene. The post-Miocene formations stretch practically horizontally. Differentiated movements gra-

Card 1/3

On the latest tectonic movements of ...

S/519/60/000/008/023/031
D051/D113

dually weakened and general planation began once more but, however, did not establish a peneplain. The pliocene basaltic flows did not engulf the axial sections of mountainous structures which emerged like inselbergs from the basalt sheet. The lower basalt surface marks the old relief, the upper layers gradually assuming a sloping position and the top layers being practically horizontal. In the south, the basalt sheet surface shows collapsed volcanic cones along an old mesozoic fault. A close connection between centers of basalt discharge and lines of intermittent faults could be observed. In this respect, olivine-pyroxene inclusions discovered by the authors in different lavas and basalts are important. Preliminary data concerning their spectral analysis are given. Uplifts in the concerned area occurred towards the end of the Pliocene and are still occurring. According to G. P. Gershkov the territory is located in a zone of seismic intensities 6 and 7. It is stated, that this activity is related to recent intermittent faults located on the edges of large depressions and stretching submeridionally and sublatitudinally. Scientists A. Z. Lazarev, Ya. Ye. Pashchenko, G. M. Vlasov, P. N. Kropotkin, B. M. Shtempel', A. M. Smirnov, N. A. Lebedeva, V. I. Bu

Card 2/3

On the latest tectonic movements of ...

S/519/60/000/008/023/031
D051/D113

and G. S. Ganeshin are mentioned. There are 1 figure and 15 references: 13 Soviet and 2 non-Soviet. The English-language references are: H. Kuno, Plateau Basalt - Lavas of Eastern Manchuria. Proc. 7-th Pac. Sci. Congr., 2, 1953; C. S. Ross, M. D. Foster and A. T. Myers. Origin of Dunites and of Olivine - Rich Inclusions in Basaltic Rocks. The American Mineralogist, No 9-10, 1954.

ASSOCIATION: Dal'nevostochnyy filial AN SSSR (Far Eastern Branch of the AS USSR)

Card 3/3

DENISOV, Ye.P.; NIKONOVA, R.I.

Recent tectonic movements in the southern Maritime Territory and adjacent regions. *Bul.MOIP.Otd.geol.* 35 no.2:28-37. Mar-Apr '60.
(MIRA 14:4)

(Maritime Territory--Geology, Structural)

DENISOV, Ye.P.

Age of blanket basalts in the southern part of the Maritime Territory.
Dokl. AN SSSR 136 no. 1:167-168 Ja '61. (MIRA 14:5)

1. Dal'nevostochnyy filial Sibirskogo otdeleniya AN SSSR.
Predstavleno akademikom D.V. Malivkinym.
(Maritime Territory--Basalt)

SAKHNO, V.G.; DENISOV, Ye.P.

Origin of the inclusions of ultrabasite rocks in basalts in the southern part of the Far East. Izv. AN SSSR, Ser. geol. 28 no. 8: 43-55 Ag '63, (MIRA 17:2)

1. Dal'nevostochnyy geologicheskyy institut Sibirskogo otdeleniya AN SSSR, Vladivostok.

SECHMELEV, V.N.; YELISSEYENKO, L.G.; DENISOV, Ye.F.; KUMSH, A.A.

Measuring X-ray photoemission from metals by means of open type
secondary-electron multipliers. Prib. i tekhn. eksp. 9 no.6:114-
118 N-D '64. (MIRA 18:3)

1. Leningradskiy gosudarstvennyy universitet.

DENISOV, Ye.P.

Some characteristics of basaltoids with ultrabasic rock
inclusions. Geol. i geofiz. no.4:168-176 '65.

(MIRA 18:8)

1. Dal'novostochnyy geologicheskii institut Sibirskogo otdeleniya
AN SSSR, Vladivostok.

L 42296-66 FWT(1)/T LJP(c)

ACC NR: AP6022499

SOURCE CODE: UR/0054/66/000/001/0057/0068

AUTHOR: Denisov, Ye. P.; Rumsh, M. A.

ORG: none

TITLE: Determination of the characteristics of the movement of the electron fluxes in a solid body by the method of the external x ray photoeffect ^{3b}

SOURCE: Leningrad. Universitet. Vestnik. Seriya fiziki i khimii,
no. 1, 1966, 57-68

TOPIC TAGS: electron flux, photoeffect, x ray photography

ABSTRACT: The article gives a calculation of the extrapolated and maximum ranges of photoelectrons from the experimental values of the quantum yield for normal and inclined incidence of the x-rays on the photocathode. After a short introduction, the article proceeds to a discussion of the basic principles determining the propagation of electron fluxes in a solid body, and then goes on to a quantitative calculation of the quantum yield of photoelectrons. Calculated results using the mathematical theory developed in the article are listed in a table and are found to be in agreement with the data of other authors.

Card 1/2

UDC: 535.215.1

↓ 42296-66

ACC NR: AP6022499

Orig. art. has: 27 formulas, 7 figures and 1 table.

SUB CODE: 20/ SUBM DATE: 16Jun65/ ORIG REF: 010/ OTH REF: 007

Card 2/2

bdh

DENISOV, Ye. T.

USSR/Chemistry - Physical Chemistry

Card 1/1

Authors : Berszin, I. V., and Denisov, E. T.

Title : Basic products of liquid-phase oxidation of cyclohexane with atmospheric oxygen and the role of these products in processes of phase-formation

Periodical : Dokl. AN SSSR, 97, Ed. 2, 273 - 275, July 1954

Abstract : Two layers (upper and lower) are formed during the oxidation of cyclohexane with atmospheric oxygen: the upper layer represents a solution of reaction products in cyclohexane; the lower layer consists of liquid oxidation products and a considerable amount of solid acids. Quantitative separation of upper layer products showed that 95 mol. % of all alcohols consisted of cyclohexanol and 97 mol. % of all carbonyl compounds consisted of cyclohexane. The lower layer contained the same products plus adipic and formic acids. Five references. Tables.

Institution : The M. V. Lomonosov State University, Moscow

Presented by : Academician N. N. Semenov, March 20, 1954

Denisov, Ye. T.
USSR/Physical Chemistry - Kinetics, Combustion, Explosions, Topo-
chemistry, Catalysis.

B-9

Abs Jour: Referat. Zhurnal Khimiya, No 3, 1958, 7210.

Author : I.V. Berezin, Ye. T. Denisov, N.M. Emanuel'.

Inst : Academy of Sciences of USSR.

Title : Kinetics and Chemism of Cyclohexane Oxydation in Liquid Phase
by Oxygen from Air under Pressure.

Orig Pub: in symposium: Vopr. khim. kinetiki, kataliza i reaktsionnoy
sposobnosti, M., izd-vo AN SSSR, 1955, 273-291.

Abstract: Cyclohexane (I) oxidation was carried out with O_2 from the air
in an autoclave installation at temperatures from 135 to 155°
and under the pressure from 10 to 100 atm. During the reaction
course, samples were taken and analyzed for cyclohexanone (II),
cyclohexanol (III) and cyclohexyl peroxide (IV) contents, and
the total contents of acids (V) and esters (VI); waste gases
were analyzed for O_2 and CO_2 . The oxidation reaction of I has

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USSR/Physical Chemistry - Kinetics, Combustion, Explosions, Topo-chemistry, Catalysis.

B-9

Abs Jour: Referat. Zhurnal Khimii, No 3, 1958, 7210.

an autocatalytic character; the kinetic curves of II, III and IV have the same shape and pass through a maximum, and the concentrations are $II > III > IV$ along the total reaction duration. After a rapid rise at the reaction start the rate of O_2 absorption remains nearly constant for some time, after which it starts slowly to drop. V and VI appear later than other products. Traces of aldehydes were detected at great depths. The activation energy according to the O_2 and IV curves is 27.2 and 29 kcal per mole correspondingly. The maximum concentrations of II, III and IV rise with the temperature rise. Additions of II (4.5, 12.5%) and butyraldehyde (0.8%) accelerate the oxidation of I very much. An addition of IV, as well as of the mixture of II, III and IV in concentrations produced at the reaction, increase the oxidation rate of I, the autocatalytic character of the kinetic curves is preserved, which indicates the existence also of

Card : 2/4

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USSR/Physical Chemistry -- Kinetics, Combustion, Explosions, Topo-chemistry, Catalysis.

B-9

Abs Jour: Referat. Zhurnal Khimiya, No 3, 1958, 7210.

other intermediate products responsible for the self-acceleration of I oxidation. The study of the IV dissociation showed that it proceeded at 135° in a steel autoclave according to the first order with constants of 0.48 hour⁻¹ (0.39 M in pure I), 0.52 hour⁻¹ (0.06 M of IV + 0.2 M of II), and 0.6 hour⁻¹ (in oxidized I medium) and produced an equimolecular mixture of II and III. The authors assume that the main amount of II is produced by the dissociation of the hydroperoxide radical, and that III is obtained at the expense of the recombination of the hydroperoxide radical with OH with the liberation of O₂. IV decomposes with formation of caprone and -oxycaprone aldehydes, which oxidize at a great rate to corresponding acids. The formation of adipic acid, (VII), the final reaction product,

Card : 3/4

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DENISOV, Ye. T

DENISOV, Ye. T.: "The kinetics of the catalytic oxidation of cyclohexanes from the point of view of the chain theory of degenerate branches."
Moscow Order of Lenin and Order of Labor Red Banner State University
M. V. Lomonosov. Chemistry Faculty. Chair of Chemical Kinetics.
Moscow, 1956. (Dissertation For the Degree of Candidate in Chemical Science.)

Knizhnaya letopis'
No 32, 1956. Moscow.

Denisov, YE. T.

✓ Kinetic characteristics of cyclohexane oxidation in the presence of cobalt stearate. (E. T. Denisov and N. M. Emanuel (M. V. Lomonosov State Univ., Moscow). Zh. fiz. khim. 51, 2527-2530 (1977). The C₆H₁₂ oxidation with Co stearate as catalyst was studied in an autoclave at 115-130° with an equimol. N₂ + O₂ mixt. at 30 atm. pressure. The reaction proceeds initially in a macroscopic range, and the reaction products formed accelerate the further C₆H₁₂ oxidation. The smaller amt. of the catalyst remaining in the soln. after the initial macroscopic stage maintains the proportion of the product and the rate of the process characteristic of the catalytic oxidation. At greater oxidation depths the Co(II) salts begin to act as neg. catalysts. Removal of the Co salts from the reaction zone results in the oxidation proceeding principally to the formation of cyclohexanone and limits its concn., which is markedly higher than in either the catalyzed or uncatalyzed reactions. W. M. Sternberg.

KM
MT

Denisov, Ye. T.

USSR/Physical Chemistry - Kinetics, Combustion, Explosions, Topo-chemistry, Catalysis.

B-9

Abs Jour: Referat. Zhurnal Khimiya, No 2, 1958, 3855.

Author : Ye. T. Denisov, N.M. Emanuel'.

Inst : Moscow State University.

Title : Mechanism of Catalysis by Cobalt Stearate at Initial Period of Cyclohexane Oxidation.

Orig Pub: Zh. fiz. khimii, 1956, 30, No 11, 2499 - 2509.

Abstract: At the beginning of cyclohexane (I) oxidation reaction catalyzed by cobalt stearate at 90 to 110° in an autoclave equipment (Berezin I.V., Dissertatsiya, MGU, 1953) a rapid transition of Co^{2+} into Co^{3+} takes place with the formation of insignificant amounts of alcohol and ketone. Later a period of a retarded reaction occurs, after which the formation process of Co^{3+} and oxidation products is resumed at a great speed. Additions of cyclohexanone (0.6mmole per lit) to the initial I result in an increased yield

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USSR/Physical Chemistry - Kinetics, Combustion, Explosions, Topo-chemistry, Catalysis.

B-9

Abs Jour: Referat. Zhurnal Khimiya, No 2, 1958, 3855.

of the initial stage products; additions of cyclohexanol (3.35 m-mole per lit) increase the duration of the retarded reaction. If St_2Co containing crystallization water was added to I, the transition of Co^{2+} into Co^{3+} and the initiation of the oxidation process do not take place. The authors think that in the initial oxidation period a rapidly retarded macroscopic initiating stage takes place, in which stage Co^{2+} converts into Co^{3+} and the latter catalyzes the further process course. Experiments with different St_2O concentrations and with additions of Co^{2+} to the developed reaction indicate that Co^{2+} retards the reaction. In the opinion of the authors, initiating is not connected with the reaction between St_2O and peroxide, but it occurs with the participation of the St_2CoO_2 complex with I.

Card : 2/2

-8-

7
Gaseous initiation by nitrogen dioxide in oxidation of cyclohexane in the liquid phase. R. T. Gerasimov and V. M. Emanuel (M. V. Lomonosov State Univ., Moscow). *Dokl. Akad. Nauk*, 31, 1268-70 (1987). — The kinetics of the formation of intermediate products and the initiator effect during the initial stage in the chain reaction $RH \rightarrow P \rightarrow K$ were examined in the light of the theory of degenerate branching. The conditions were detd. under which stopping the initiation no longer affected the kinetic curve for the production of the intermediate. NO_2 sharply increased the velocity of oxidation of cyclohexane (I) to cyclohexanone and adipic acid at 110–120°. Interruption of the NO_2 supply retarded the oxidation. Conditions could be found, however, when a short admission of the initiator produced no breaks in the kinetic curve after an interruption in its supply. The formation of cyclohexyl nitrate during the oxidation of I initiated with NO_2 was demonstrated spectroscopically. HNO_2 was formed during the low-temp. initiation. The combined action of NO_2 and Co stearate resulted in an addnl. acceleration of the reaction, especially during the early stages. W. M. Starchuk

Distr: 4843

Distr: 4843/483d

Autoretardation of slowly developing chain reactions.
E. T. Denisov. *Dokl. Akad. Nauk SSSR*, 31, 1481-82, 1987.
The accumulation of oxidation products in a hydrocarbon
oxidizing medium should change the mean values of the
rate constants of the reaction between the radical and the inter-
mediate products. The consts. were correlated with the
concentrations of the reaction products. The schematic representa-
tion of an unbranched chain reaction was examined. In the
light of changes in the radical activity during the reaction.
With the accumulation of the less active radicals the experi-
mental law may be initiated in a particular form, but on the
appearance of the more active radicals the unbranched chain
reaction initiates the kinetics of the degenerate chain branch-
ing. The kinetics of various chain-branching reactions may
imitate the kinetics of unbranched chain reactions. In
addn. of certain substances in the oxidation of various hydro-
carbons and the degeneration of the low-temp. oxidation of
liquid hydrocarbon was suggested. The compn. of the oxida-
tion products affects the kinetic equilibrium of the inter-
mediate products responsible for the degenerate branching.

W. M. Stenberg.

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3
2

1/1

Denisov, Ye. T.

20-3-28/52

AUTHORS: Emanuel', N. M. , Denisov, Ye. T.

TITLE: Theoretical Possibility of Oxidation of Benzene to Phenol
in the Liquid Phase (O printsipial'noy vozmozhnosti zhidkofaznogo
okisleniya benzola v fenol)

PERIODICAL: Doklady AN SSSR, 1957, Vol. 117, Nr 3, pp. 458 - 461 (USSR)

ABSTRACT: The authors here endeavor to determine the oxidation of benzene at temperatures of from 230 - 270° and at a pressure of 50 atmospheres. Experiments were carried out in an autoclave device for the oxidation of hydrocarbons in the liquid phase under pressure. At each experiment 200 mm of benzene were introduced into the reactor. Oxidation was carried out by the oxygen of a nitrogen oxygen mixture with the composition 1 : 1. During this process samples were taken of oxidized benzene and were analyzed with respect to their phenol content. With a photocalorimeter also the optical density of the oxidized benzene was measured. At 250° oxidation of the benzene in the liquid phase takes place with noticeable rapidity. With the oxidation of benzene phenol and resins are produced. The kinetic curve of the accumulation of phenol is of S-like character. However, the maximum concentration of phenol in this process amounts to only 0,16 mol percent. In the oxidation of benzene with cobalt

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20-3-28/52

**Theoretical Possibility of Oxidation of Benzene to Phenol
in the Liquid Phase**

stearate this catalyzer directs the reaction into the direction of the condensation of benzene with the production of soot; only small quantities of phenol are produced on this occasion. Small quantities of easily oxidizable substances such as cyclohexane and cyclohexanon accelerate the oxidation of benzene. The corresponding kinetic curves are given. The experimental data obtained here concerning the oxidation of benzene tend to show that this process is a chain-like degenerated, ramified, self-decelerating reaction. The experimental data agree well with a mechanism, which is described in detail. The present paper proves that, in principle, it is possible to attain the oxidation mentioned in the title at temperatures that are near critical temperature. The principle of gas initiation applied on this occasion furnished the best results. The processes for the removal of the self-slowing-down of the processes will have to be examined. There are 3 figures and 4 references, 3 of which are Slavic.

Card 2/3

20-3-28/52

**Theoretical Possibility of Oxidation of Benzene to Phenol in the
Liquid Phase**

ASSOCIATION: Institute for Chemical Physics AN USSR
(Institut khimicheskoy fiziki Akademii nauk SSSR)

PRESENTED: May 15, 1957, by N. N. Semenov, Academician

SUBMITTED: May 15, 1957

AVAILABLE: Library of Congress

Card 3/3

AUTHORS: Denisov, Ye.T., Emanuel', N.M. (Moscow) 74-27-4-1/8

TITLE: The Effective Mechanism of the Inhibitors in Chain Reactions of the Liquid Oxidation Phase (Mekhanizm deystviya ingibitorov v tsepnykh reaktsiyakh zhidkofaznogo okisleniya)

PERIODICAL: Uspekhi Khimii, 1958, Vol. 27, Nr 4, pp. 365-402 (USSR)

ABSTRACT: The report begins by dealing with the importance of inhibitors and the research work carried out in this connection during the past decades. Mention is made of the works by Muro and Dyufres (Ref 7) on antioxidation. After the function of inhibitors had, in their general outlines, become known and the chain theory supplied relatively simple formulae for the description of slowing-down effects theoretical interest in inhibitors began to die down. It was only recently that one of the authors of this paper pointed out that in numerous cases oxidation processes have a far more complicated mechanism than that of the slowly growing and ramified chain avalanche. The present survey is devoted to the analysis of the chemical effective mechanism of inhibitors and to the theoretical interpretation of and the particular effect exercised by inhibitors on the basis of the theory of chain reactions with degenerated

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The Effective Mechanism of the Inhibitors in Chain
Reactions of the Liquid Oxidation Phase

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ramifications as developed by Semenov. The report is divided into the following parts: The chain mechanism of the oxidation of hydrocarbons. The "chain-interrupting" chemical effect exercised by inhibitors; on the separation of the H-atom from the molecule of the admixture InH; on the connection of the free radical with the molecule of the admixture Q; the mechanism of the inhibiting effect of phenols; the mechanism of the inhibiting effect of amines. The next chapter deals with the kinetic characteristic of the effect exercised by inhibitors: 1.) The theory of the effect produced by strong inhibitors. 2.) The theory of the effect produced by weak inhibitors. - The following chapter deals with antioxidants which exercise a retarding effect upon the velocity of degenerated ramification. Mention is made in this connection of the destructive effect exercised by sulfides upon hydroperoxides, of the problem concerning the modification of the kinetic curve of oxidation of hydrocarbon, of the slowing-down effect produced with respect to the oxidation process of alkaline substances and acids. In conclusion the report deals with the joint effect produced by 2 antioxidants. In this connection the fact is stressed that the joint

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effect produced by two substances which are able to destroy peroxides can often produce a greater effect than may be assumed on the strength of the rule of additivity. There are 10 figures, 6 tables, and 81 references, 23 of which are Soviet.

1. Chain reactions--Inhibition 2. Oxidation inhibitors--Analysis

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DSN/50V, YE. T.

AUTHOR: Denisov, Ye. T.

76-1-15/32

TITLE: The Specific Action of Inhibitors on Degenerate Branching Chain Reactions (Osobennosti deystviya ingibitorov na tsepnyye vyrozhdennno-razvetvlennyye reaktsii).

PERIODICAL: Zhurnal Fizicheskoy Khimii, 1953, Vol. 32, Nr 1, pp. 99-108 (USSR)

ABSTRACT: By means of the chain theory the various processes connected with the influence of inhibitors on chain reactions with degenerate branches are investigated. Some facts regarding the effect of inhibitors on the oxidation of liquid hydrocarbons are explained. Based on a general investigation of the influence of various inhibitors a kinetic explanation of the conceptions on force and effectiveness of the slowing-down effect of inhibitors are given. The hydrocarbon oxidation processes are degenerate branching chain reactions. The slowing down effect of inhibitors is dependent on the -ir interaction with free radicals. This leads to a slowing down of the chain extension reaction. Three possible processes of the interaction are shown. The author states that a weakening of the slowing down effect of some inhibitors with

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The Specific Action of Inhibitors on Degenerate Branching Chain Reactions 76-1-15/32

their introduction in to the already developing process of degenerate branching chain reaction takes place independent from inhibiting, from the character of the disconnection of the chains in reaction. This characteristic makes a difference between the degenerate branching chain reactions the non-branching chain reactions (the latter are slowed down when the inhibitors are introduced at the beginning of the reaction, as well as when the introduction takes place during a reaction already in progress)(ref. 8). The cause of the weakening of the slowing down effect of inhibitors on the degenerate branching chain reactions with the development of the latter is that the reactions develop automatically. The reaction velocity with degenerate branchings is determined at any moment by the concentration of the substance which injects the chains and forms during reaction. The inhibitor slows down the formation of this substance. The slowing down is not only determined by the intensity of the slowing down effect, but also by its duration. The intensity of the slowing down effect of an inhibitor is determined by the ratio between

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the velocity constant of the reaction of the radical formed of the inhibitor and the radical effecting the oxidation with the hydrocarbon. The smaller this ratio is the stronger is the inhibitor. The effectiveness of the slowing down effect is determined by the magnitude of the constant of reaction velocity of the radical effecting oxidation with the inhibitor. The greater it is the greater is the constant. The explanation for the opposite effect on the oxidation of various hydrocarbons with the addition of some substances is given. The activity of the radicals through which the oxidation of hydrocarbon takes place changes from one hydrocarbon to the other. The radicals forming with the oxidation from such related hydrocarbon compounds, as there are alcohols or acids, apparently do not differ much as regards their activity from those radicals forming with the oxidation of hydrocarbons. Therefore cases are easily possible where the radicals forming with the oxidation of such a substance, are less active than the respective radicals of a hydrocarbon, but much more active than radicals which effect the oxidation of another hydrocarbon. In the first case an addition of this substance will slow down oxidation, in the

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The Specific Action of Inhibitors on Degenerate Branching 76-1-15/32
Chain Reactions

oxidation, in the second case it will accelerate it. In the end the author shows that when a weak inhibitor is introduced to a reaction already in progress the slowing down of the chain reaction could occur because of the change of the composition of radicals in the course of the chain process. There are 3 figures, and 13 references, 9 of which are Slavic.

ASSOCIATION: Moscow State University imeni M. V. Lomonosov.
(Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova)

SUBMITTED: October 8, 1956

AVAILABLE: Library of Congress

Card 4/4

AUTHOR:

Denisov, Ye. T.

Doc/ 76-32-6-13/46

TITLE:

On the Participation of Salt Catalysts in the Chain Propagation Reaction of the Liquid Phase Hydrocarbon Oxidation (Ob uchastii solevykh katalizatorov v reaktsii prodolzheniya tsepi pri zhidkofaznom okislenii uglevodorodov)

PERIODICAL:

Zhurnal fizicheskoy khimii, 1958, Vol. 32, Nr 6, pp. 1269 - 1276 (USSR)

ABSTRACT:

Owing to the complicated nature of the problem and insufficient experimental evidence various standpoints have hitherto been adopted papers concerning the mechanism of the catalysis with metal salts and organic acids. The results of the catalytic oxidation of cyclohexane lead to the assumption that processes of chain propagation are caused by such catalysts. In the present paper factors are pointed out on the strength of the theory of chain reactions with degenerate ramifications indicating such a reaction. New experimental data are evaluated and the correctness of the assumptions is proved. It is found that a reaction of the free radicals with hydrogen peroxide must be assumed apart from the transformation of the ROO-radicals in hydrogen peroxide. The

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On the Participation of Salt Catalysts in the Chain ~~76~~76-32-6-13/46
Propagation Reaction of the Liquid Phase Hydrocarbon Oxidation

scheme of reaction derived herefrom, however, is unable to explain all experimental evidence obtained. It appears, among other things, that an interaction of the catalyst with the ROO-groups takes place under the formation of another radical, as for example OH and molecular products which differ from hydrogen peroxide as do a ketone or an alcohol. Proceeding from this assumption corresponding equations are derived. Experiments were conducted, determining the content of hydrogen peroxide, ketone and alcohol. The kinetic curves showed that all three products are formed in parallel in the presence of salt catalysts. Thus the assumption is proved that an interaction of the catalyst with the radical ROO takes place under the formation of a new radical, of alcohol and of ketone. Salts with cations containing smeared electrons must react particularly actively with the free radicals. This is substantiated by the experimental evidence concerning the oxidation of cyclohexane with cobalt and manganese stearate, in which the production of hydrogen peroxide is particularly small in the beginning. There are 4 figures, 1 table, and 11 references, 6 of which are Soviet.

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On the Participation of Salt Catalysts in the Chain SOV/76-32-6-13/46
Propagation Reaction of the Liquid Phase Hydrocarbon Oxidation

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova
(Moscow State University imeni M. V. Lomonosov)

SUBMITTED: January 18, 1957

1. Hydrocarbons (Liquid)--Oxidation 2. Metal salts--Catalytic
properties 3. Organic acids--Catalytic properties

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5(4)

AUTHORS: Denisov, Ye.T., Emanuel', N. M.

SOV/76-32-10-21/39

TITLE: The Liquid Phase Oxidation of Benzene to Phenol at Temperatures Close to the Critical Point (Oksleniye benzola v fenol v zhidkoy faze pri temperaturakh, blizkikh k kriticheskoy)

PERIODICAL: Zhurnal fizicheskoy khimii, 1958, Vol 32, Nr 10, pp 2374 - 2382 (USSR)

ABSTRACT: In an earlier paper (Ref 1) it was pointed out that a series of high-temperature oxidations can be carried out in the gas phase at low temperatures, and in the liquid phase. In the present paper the oxidation of liquid benzene is carried out at 230-270° (especially at 250°) and at a pressure of 50 atmospheres absolute pressure. An autoclave serving for the investigation of the kinetics of processes in liquid phase (Ref 5) was used. Benzene oxidizes in the liquid phase rather rapidly at 250°; phenol and resins are formed as reaction products. An addition of 2 mol% cyclohexane causes an acceleration in the process, whereas 1 mol%

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Temperatures Close to the Critical Point

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cyclohexanone shows a still stronger effect. The addition of 0,15 mol% cobalt stearate led to the opposite effect, i.e. a small formation of phenol took place; however, with a large formation of soot. Experiments carried out with gas injections yielded the best results when nitrogen dioxide was used. Nitrobenzene was qualitatively determined among the oxidation products in this case. The interruption of the gas passage leads to a slowing down of the reaction so that a stimulation by nitrogen dioxide should take place throughout the oxidation process. It is assumed that benzene oxidizes also in the liquid phase according to the chain mechanism. The maximum phenol formation depends on the self-impedance of the benzene reaction. The present reaction is considered in relation to the theory of chain reactions by N.N.Semenov (Ref.9), and the experimental data obtained are compared. The self-impedance of the chain reaction is explained by the accumulation of products that inhibit the reaction by an exchange

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of active radicals against less active ones. According to a scheme the weakly active free radicals react with intermediate products and the maximum concentration of the intermediate products is lower the higher the inhibition by the oxidation products. On the other hand, the final product will be formed at a maximum velocity in the case that the maximum concentration of the intermediate products is obtained. There are 6 figures and 10 references, 8 of which are Soviet.

ASSOCIATION: Akademiya nauk SSSR, Institut khimicheskoy fiziki (AS
USSR, Institute of Chemical Physics)

SUBMITTED: May 15, 1957

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DENISOV, YE T

PHASE I BOOK EXPLOITATION

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Akademiya nauk SSSR. Institut khimicheskoy fiziki

Okisleniye uglevodorodov v zhidkoy faze; sbornik statey (Oxidation of Hydrocarbons in the Liquid Phase; Collection of Articles) Moscow, Izd-vo AN SSSR, 1959. 334 p. Errata slip inserted. 2,200 copies printed.

Ed.: N. M. Emanuel', Corresponding Member, Academy of Sciences USSR; Ed. of Publishing House: K. M. Dymayev; Tech. Ed.: I. F. Kuz'min.

PURPOSE: This collection of articles is intended for chemists interested in hydrocarbon oxidation reactions, particularly for those specializing in petroleum fuels.

COVERAGE: This collection of 35 articles represents the results of investigations over a period of several years on problems of hydrocarbon oxidation. The authors present their own theoretical and experimental data and also draw from current literature. No personalities are mentioned. References accompany most of the articles.

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Oxidation of Hydrocarbons in the (Cont.)

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Knorre, D.G. [Institute of Chemical Physics]. Some Elementary Stages in the Liquid-Phase Oxidation of Hydrocarbons

46

This study, based on data from the literature indicates that hydroperoxide formation is the initial stage in the formation of stable hydrocarbon oxidation products. Reaction activation energies and reaction rates are computed both theoretically and experimentally.

Denisov, Ye.T. [Moskovskiy gosudarstvennyy universitet imeni M.V. Lomonsova (Moscow State University imeni M.V. Lomonsov)]. Influence of Products of a Slowly Developing Chain Reaction on the Length of the Unbranched Chain

55

The influence of oxidation product concentration on the length of side chains is investigated. On this basis, a number of phenomena observed during the liquid-phase oxidation of hydrocarbons is explained: self-retardation of the oxidation process, rectification of the kinetic curves during low-temperature oxidation, the increase in effective activation energy with lowered temperature, etc.

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Oxidation of Hydrocarbons in the (Cont.)

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Denisov, Ye.T. [Moscow State University imeni M. V. Lomonosov].
Characteristics of the Action of Inhibitors on Side-Chain Decomposition
Reactions

66

Ivanov, K.I., and Ye.D. Vilyanskaya [Vsesoyuznyy teplo tekhnicheskii nauch-
no-issledovatel'skiy institut imeni F. E. Dzerzhinskogo (All-Union Heat
Engineering Scientific Research Institute imeni F. E. Dzerzhinskiy)].
Effect of Inhibitors on the Kinetics of the Autoxidation of Hydro-
carbons

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The authors investigate the effect of various inhibitors on the
autoxidation of hydrocarbons from petroleum crudes, as well as
various stages in the development of the oxidation process.

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Oxidation of Hydrocarbons in the (Cont.)

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polyvalent metal salts in the decomposition of peroxides and the oxidation of hydrocarbons is discussed.

Blyumberg, E.A., Z.K. Mayzus, and N.M. Emanuel' [Institute of Chemical Physics]. Liquid-Phase Oxidation of n-Butane at Near-Critical Temperatures and Pressures

125

The authors discuss the kinetics and chemistry of a purportedly new method for liquid-phase oxidation of n-butane. Initiating the reaction with NO_2 and catalyzing with CoSt_2 resulted in a shorter induction period by increasing the initial rate of chain growth. Acetic acid and methyl ethylketone are the principal products of the reaction.

Denisov, Ye.T. [Moscow State University imeni M.V. Lomonosov] Kinetics of Cyclohexane Oxidation Catalyzed by Cobalt Stearate

136

The author finds that the catalytic action of cobalt salts (stearates) both breaks down and initiates chain growth during the oxidation of cyclohexane. The relationship between these functions is substantially changed as the reaction develops.

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SOV/62-59-12-6/43

AUTHOR: Denisov, Ye. T.

TITLE: Causes for Changes in Concentration of the Intermediate Product in the Course of Chain Reaction

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 12, pp 2100-2111 (USSR)

ABSTRACT: During oxidation reactions with degenerate branching, the concentration of the molecular intermediate product (hydroperoxide, ketone, aldehyde), after reaching a maximum, often starts to decrease rapidly. The author considered possible cases in which the concentration of the intermediate in the reaction $RH \rightarrow P \rightarrow K$ (where RH is starting compound, P is intermediate, K is final product) is decreasing: (1) reaction, in which the intermediate is formed and consumed by a chain process; (2) the intermediate is consumed by a nonchain process, in which the accumulating products alter the consumption rate of the intermediate; (3) formation of ionic products

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Causes for Changes in Concentration of the
Intermediate Product in the Course of Chain
Reaction

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takes place, catalyzing ionic dissociation of the intermediate. Two main causes for the decrease of intermediate-product concentration are: (1) change of radical composition and their activity in the course of reaction. When the intermediate is formed and consumed by a chain process, its concentration changes when the relative reactivity of the radicals changes, i.e.

$\frac{k_{01}}{k_{\infty}} \neq \frac{k_{11}}{k_{10}}$, or $\frac{k_1}{k_0}$ ratio is not constant.

Here k_0 and k_1 are rate constants of the radicals with RH and P, respectively, 1 denotes free radical (from 0 to 1); 0 denotes RH; 1 denotes P. This inequality takes place when the heats of the four reactions do not have the same sign. (2) Rate increase of the intermediate-product consumption by a nonchain process. This takes place due to accumulation of

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Causes for Changes in Concentration of the
Intermediate Product in the Course of Chain
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compounds, reacting with the intermediate, or due to accumulation of acids, which cause ionic decomposition of the intermediate. In actual oxidation processes, one may find cases in which either both, or predominantly one of the causes exist. There are 4 figures; and 16 references, 7 Soviet, 4 U.K., 5 U.S. The 5 recent U.K. and U.S. references are: J. E. Hay, N. M. Johnstone, C. F. Tipper, R. H. Williams, J. Chem. Soc., 1954, 629; E. J. Gasson, A. F. Millidge, G. S. Primavesi, J. Chem. Soc., 1954, 2161; F. H. Seubold, W. E. Vaughan, J. Amer. Chem. Soc., 75, 3790 (1953); C. F. Tipper, J. Chem. Soc., 1953, 1675; M. S. Kharach, J. S. Burt, J. Organ. Chem., 16, 150 (1951).

ASSOCIATION: Institute of Chemical Physics of the Academy of Sciences
USSR (Institut khimicheskoy fiziki Akademii nauk SSSR)

SUBMITTED: March 22, 1958

Card 3/3

5(3)

SOV/80-32-4-33/47

AUTHORS: Berezin, I.V., Denisov, Ye.T., Suvorova, S.N., Smolyan, Z.S. and Emanuel', N.M.

TITLE: The Oxidation of a Mixture of Cyclohexane and Cyclohexanol to Adipic Acid (Okisleniye smesi tsiklogeksana i tsiklogeksanola v adipincvuyu kislota)

PERIODICAL: Zhurnal prikladnoy khimii, 1959, Vol 32, Nr 4, pp 888-892 (USSR)

ABSTRACT: Production of monomers for plastics and synthetic fibers is one of the important tasks of modern chemistry. The utilization of various waste materials can contribute to the solution of this task. One of these waste materials is the mixture of cyclohexane, 80 mol.%, and cyclohexanol, 20 mol.%. The authors studied the kinetics of the oxidation of this mixture, called "anol head", with an aim of obtaining cyclohexane and adipic acid. The oxidation was carried out in an autoclave at a pressure of 20 atm by molecular oxygen at temperatures of 130 and 150°C. Kinetic curves of accumulation of the reaction products were obtained and the possibility of producing adipic acid by oxidizing the "anol head" was proven. It was shown that some peculiarities in the oxidation kinetics were determined wholly by the concentration of cyclohexanol

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SOV/80-32-4-33/47

The Oxidation of a Mixture of Cyclohexane and Cyclohexanol Into Adipic Acid

in the "anol head". The process of oxidizing "anol head" is to be carried out with continuous removal of adipic acid obtained in order to prevent its burning into lower dicarboxylic acids, and the process thereby acquires a continuous character. There are 3 sets of graphs and 7 Soviet references.

SUBMITTED: November 1, 1957

Card 2/2

5(4)

AUTHOR:

Denisov, Ye. T.

SOV/76-33-6-6/44

TITLE:

Investigation of the Oxidation of Cyclohexane by an Inhibiting Method During the Course of the Reaction (Izucheniye oksidatsiya tsiklogeksana metodom ingibirovaniya po khodu reaktsii)

PERIODICAL:

Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 6, pp 1198-1208 (USSR)

ABSTRACT:

To characterize a chain-oxidation process it is necessary to know the chain formation rate and the chain length as well as the kinetics of the variation of both these quantities during reaction. A rather simple method of determining these quantities in the case of oxidation in the liquid phase, is that of inhibiting the reaction. There are two basic possibilities in a chain reaction with the formation of degenerated ramifications, with an intermediate and an end product. 1) The molecular intermediate product (Z), from which the degenerated ramification is originated, occurs after a chain reaction, and also decomposes after a chain reaction. 2) (Z) is formed by a chain reaction; it does not, however, decompose after a chain reaction. Both these cases are thoroughly dealt with theoretically, and it is stated that in the first case the addition of an inhibitor (I) effects a marked retardation of the accumulation of (Z), while in the second case the (I) addition causes the

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Investigation of the Oxidation of Cyclohexane by an Inhibiting SOV/76-33-6-6/44
Method During the Course of the Reaction

consumption of (Z) already in the course of inhibition; hence, the mechanism of the consumption of (Z) under pertinent reaction conditions may be interpreted on the strength of the variation of the kinetic curve of the (Z) accumulation following the addition of a strong (I). The present paper deals with the investigation of the oxidation of 200 ml cyclohexane (II) in a special autoclave system. At 140° and 30 atm pressure a nitrogen-oxygen mixture (1:1) was blown through with a velocity of 30 l/hour, with α -naphthal (III) being used as (I). Experimental results show (Figs 3-6) that (III) inhibits the formation of the ketone, of alcohol and of acids, i.e. the (II) oxidation is basically a chain reaction. The kinetic curves of the cyclohexylhydroperoxide-(IV) formation after a (I) addition (Fig 6) show that (IV) does not decompose after a chain reaction. There is no direct reaction between (III) and (IV) (Table 1). Data are supplied concerning chain initiating rate and chain length (Table 2). An explanation is given of the peculiar course of the diagram of the chain length variation during reaction, and the total activity of the free radicals governing oxidation, is found to change considerably during reaction. These changes strongly promote the increase in

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Investigation of the Oxidation of Cyclohexane by an Inhibiting SOV/76-33-6-6/44
Method During the Course of the Reaction

oxidation velocity of (II), which is observable in the course of reaction. There are 8 figures, 2 tables, and 17 references, 13 of which are Soviet.

ASSOCIATION: Akademiya nauk SSSR Institut khimicheskoy fiziki (Academy of Sciences of the USSR, Institute of Chemical Physics)

SUBMITTED: May 15, 1957

Card 3/3

5(4)

AUTHORS:

Denisov, Ye. T., Mayzus, Z. K.,

SOV/20-128-4-33/65

~~Skibida, I. P.~~, Emanuel', N. M., Corresponding Member, AS USSR

TITLE:

Kinetic Laws for Autocatalytic Reactions in Open Systems

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 4,
pp 755-758 (USSR)

ABSTRACT:

In chemical technology, the continuous process of reactions is attempted more and more, i.e. of reactions in open systems. While the kinetics of simple processes had already been investigated (Refs 2-4), no data are available on autocatalytic processes. Therefore, the continuous oxidation of cyclohexanone to adipic acid by oxygen at 130° was studied. The apparatus used permitted the automatic maintenance of the inflow of raw material and of the outflow of the reaction products. The term of "specific velocity" v is defined as the volume of the liquid initial component supplied to the unit of volume of the reaction vessel in the unit of time.

The value $\frac{1}{v}$ indicates the average duration of stay of the liquid in the reaction vessel. The content of hydrogen peroxide, adipic acid, and CO₂ in the reaction product is

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determined for different v . In the continuous process, a stationary state appears, i.e. the reaction rate and the discharge of the end product are in an equilibrium relation to each other. Figure 1 shows the dependence of the equilibrium concentration of adipic acid on v . In the transition from the periodic process to the continuous one, it is of no importance in which phase of reaction this transition takes place since the equilibrium concentration is formed corresponding to v , irrespective of the oxidation degree attained. While for simple reactions the rate rises monotonously with v , there is a different dependence for autocatalytic reactions since not only the concentration of the initial product but also that of the resulting intermediate product (hydrogen peroxide) is decisive. Figure 3 shows that the reaction rate passes a maximum at a certain v ; if v keeps on rising, the reaction rate falls since the concentration of the hydrogen peroxide becomes lower. The equation for the maximum reaction rate is written down. It is pointed out that in the continuous process, in comparison with the periodic process, a smaller amount of burning to CO_2 and H_2O

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occurs because the reaction products remain in the
reaction zone for a shorter period. There are 3 figures
and 6 references, 3 of which are Soviet.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute
of Chemical Physics of the Academy of Sciences. USSR)

SUBMITTED: June 22, 1959

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S/081/60/000/023/001/021
A005/A001

11.6200

Translation from: Referativnyy zhurnal, . Khimiya, 1960, No. 23, p. 59, # 91595

AUTHOR: Denisov, Ye. T.

TITLE: On the Effect of the Products of a Slowly Evolving Chain Reaction
on the Length of a Non-Ramified Chain

PERIODICAL: V sb.: Okisleniye uglevodorodov v zhidkoy faze. Moscow, AN SSSR,
1959, pp. 55 - 65

TEXT: The kinetic equations are derived and analyzed for the case of non-ramified and degenerated ramified chain reactions. Activity variations of the radical-carriers of the chains are taken into consideration. These variations occur in the course of the conversion because of the accumulation of reaction products in the reaction system, which react with the radical-carriers with the formation of radicals differing from the radical-carriers in their reactivity. On the basis of the results obtained, the following experimental facts are explained which can be observed at the chain oxidation of hydrocarbons: self-inhibition, rectification of the kinetic curves at low temperatures, increase of the apparent activation energy at decreasing temperature, the existence of a sharply

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S/081/60/000/023/001/021
A005/A001

On the Effect of the Products of a Slowly Evolving Chain Reaction on the Length of a Non-Ramified Chain

expressed peak in the kinetic curves of the accumulation of intermediate products, the opposite effects of additions of the same substance on the oxidation of different hydrocarbons, the difference in the effectiveness of an inhibitor depending on the conversion depth at which the inhibitor was introduced into the reaction system, the simulation of regularities in the process of a degenerated ramified reaction by a non-ramified chain reaction (and vice-versa) ✓.

G. Korolev

Translator's note: This is the full translation of the original Russian abstract.

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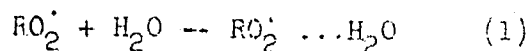
SOV/62-60-1-9/37

AUTHOR: Denisov, Ye. T.

TITLE: Concerning a Possibility of Hydrogen Bond Formation
Between a Peroxide Radical and Molecules Containing
an OH Group

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh
nauk, 1960, Nr 1, pp 54-58 (USSR)

ABSTRACT: This paper presents a theoretical substantiation
and experimental proof of the formation of a complex
hydrogen bond between a peroxide radical and molecules
containing an OH group: $ROO \dots HOX$, where X is:
H, R, FCO, RO. The rate of oxidation is determined
by the concentration and activity of the free radicals.
In the presence of compounds containing OH groups, e.g.,
water, formation of the above complex takes place:



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Concerning a Possibility of Hydrogen Bond
Formation Between a Peroxide Radical and
Molecules Containing an OH Group

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Formation of the above complex would cause a decrease in the rate of oxidation. Experiments conducted with oxidation of anhydrous cyclohexanone and cyclohexanone containing different amounts of water with a mixture of nitrogen and oxygen in a 1:1 ratio at 120°, show that addition of water to the reaction mixture decreases the rate of cyclohexanone oxidation. Inhibiting action of water indicates that the formation of the above complex takes place. There are 1 table; 2 figures; and 6 references, 1 German, 5 Soviet.

ASSOCIATION: Institute of Chemical Physics, Academy of Sciences,
USSR (Institut khimicheskoy fiziki Akademii nauk
SSSR)


SUBMITTED: March 31, 1958

Card 2/2

S/595/60/000/000/004/014
E196/E535

AUTHORS: Emanuel', N.M., Berezin, I.V. and Denisov, Ye.T.
TITLE: The oxidation of cyclohexane
SOURCE: Vsesoyuznoye soveshchaniye po khimicheskoy pererabotke
neftyanykh uglevodorodov v poluprodukty dlya sinteza
volokon i plasticheskikh mass. Baku, 1957. Baku, Izd-
vo AN Azerb.SSR, 1960, 143-156

TEXT: The kinetics of oxidation of cyclohexane were investi-
gated without using catalysts, with catalytic salts and with a
stimulating gaseous initiation. The aim of this study was to
gain more information on the oxidation of cyclohexane which is
important in the production of cyclohexanone and adipic acid for
the nylon fibre industry. A further aim was to determine the laws
governing this simple liquid phase oxidation and to apply these
laws to more complicated hydrocarbons. Without a catalyst
satisfactory velocities can be attained at pressures of 10-100 atm
and temperatures of 135-155°C. The main intermediate products
are cyclohexanone, cyclohexanol and cyclohexyl hydroperoxide. A
second liquid phase appears when the reaction mixture becomes

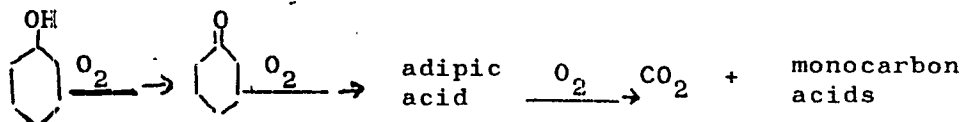


Card 1/5

The oxidation of cyclohexane

S/595/60/000/000/004/014
E196/E535

saturated with water and adipic acid, which have limited solubilities in cyclohexane. As the reaction is a chain degradation-branching reaction, no single parameter can be used to characterize it. The maximum absorption rate of oxygen is a function of temperature and obeys the Arrhenius equation, with an activation energy of 27 kcal/mol. The log of the conversion coefficient to cyclohexyl hydroperoxide over the first part of the reaction varied linearly with the inverse of the temperature, with activation energy 29 kcal/mol. For the intermediate cyclohexanone, the log maximum concentration varied linearly with the inverse of the temperature, the activation energy being 8 kcal/mol. The transformation of the intermediate products was studied by the use of radioactive carbon as marker and the following sequence was found



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The oxidation of cyclohexane

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E196/E535

In glass vessels the hydroperoxide breaks down equally into cyclohexanol, formed entirely by the decomposition of cyclohexyl hydroperoxide, and cyclohexanone, from decomposition of the hydroperoxide and oxidation of cyclohexanol. Adipic acid is formed exclusively by oxidation of cyclohexanone whilst the esters are formed by direct esterification of the adipic acid with cyclohexanol. In a steel vessel, however, cyclohexanone is also formed by decomposition of the cyclohexyl hydroperoxide radical. In the reaction with catalyzing salts, cobalt stearate dissolved in cyclohexane was used as catalyst. During the reaction, the cobalt changes into the trivalent state, and after a few minutes at 130°C the concentration of Co(III) becomes constant, then begins to decrease until after about 1.5 hours it is all once more in the divalent state. With the appearance of adipic acid the cobalt begins to precipitate as cobalt adipate, but part of the catalyst remains in solution throughout the reaction. The catalyzed and non-catalyzed oxidations differ as regards the reaction rate and concentrations of the intermediate products. Experiments with different concentrations of

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The oxidation of cyclohexane

S/595/60/000/000/004/014
E196/E535

the catalyst (0.06 to 0.00023 mol %) showed that the higher the amount of catalyst, the faster the rate of reaction, demonstrating that, in the initial periods, it is a chain reaction whose rate of initiation is proportional to the concentration of dissolved catalyst. Similar results were obtained using cobalt adipate. The catalyst has thus two functions - initiation of the reaction and regulation of the proportions of the products. The rate of absorption of oxygen in the uncatalyzed reaction remains constant after the induction period; in the catalyzed reaction it rises to a maximum and ^{then} decreases to a constant value which is less than that of the uncatalyzed reaction. This suggests a self-delaying action. To confirm this supposition the catalyst was removed from the reaction zone some time after initiation and the final constant velocity attained was found to be higher than for the uncatalyzed reaction. A new method of stimulating liquid phase oxidation, using NO_2 , was studied. The air was saturated with NO_2 (0.4%) at a rate of 50 litres/hr. At 140°C the reaction was markedly accelerated. The method was also tried in combination with cobalt stearate catalyst. A table is

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The oxidation of cyclohexane

S/595/60/000/000/004/014
E196/E535

included which gives yields of acid and ketone for the various methods of oxidation. A mathematical analysis of the reaction is made on the assumption that it is a simple chain reaction with a single intermediate and a single final product; the chain is assumed to be broken by recombination of the free radicals. Academicians B. A. Kazanskiy, G. S. Landeberg and N.N. Semenov are mentioned in the paper. There are 10 figures and 2 tables.

Test	Depth of oxidation	Yield of acid, %	Yield of ketone, %	<u>Table</u>
Autooxidation	14.8	30	37	
Oxidation with St_2Co	18.5	58	23	
Oxidation with NO_2	19	57	22	
Oxidation with $\text{St}_2\text{Co} + \text{NO}_2$	22	51.5	27	

Card 5/5

DENISOV, Ye.F.

Oxidation of acetone, initiated by benzoyl peroxide. Izv.AN
SSSR Otd.khim.nauk no.5:812-815 My '60. (MIRA 13:6)

1. Institut khimicheskoy fiziki Akademii nauk SSSR.
(Acetone) (Benzoyl peroxide)

S/074/60/029/012/003/004
B013/B078

AUTHORS: Denisov, Ye. T., Emanuel', N. M.

TITLE: Catalysis With Metals of Variable Valence in Oxidation
Reactions in the Liquid Phase

PERIODICAL: Uspekhi khimii, 1960, Vol. 29, No. 12, pp. 1409 - 1438

TEXT: This is a survey of experimental data published over the past decade concerning oxidation processes in the liquid phase under the catalytic action of metals of variable valence. The review offers a broad outline of mechanisms by which the salt-catalysts act upon the oxidation of aldehydes and hydrocarbons. The existing experimental material concerning the catalytic oxidation of organic compounds (Refs. 4-6, 8, 10, 16-49; Figs. 1-6; Tables 1-3) indicates that catalysts of variable valence take an active part in the initiation of chains. The basic difference between these catalysts and the peroxides as well as azo compounds is that each molecule of the catalyst may repeatedly participate in the initiation of a chain by causing the transformation of molecular products into free radicals. The mechanism of the initiation of chains, however, has not been

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Catalysis With Metals of Variable Valence in S/074/60/029/012/003/004
Oxidation Reactions in the Liquid Phase B013/B078

investigated more closely. A further function of catalysts of variable valence, e.g., the tearing of chains has been examined in Refs.11, 20-23, 27, 38, 50-52. (Tables 7-11). Such a reaction takes place when the catalyst reacts with free radicals. The inhibiting effect of the catalysts is in most cases non-apparent due to the stronger acting effect of initiation. A thorough study of the inhibiting effect of catalysts is still in its initial stage. Physico-chemical properties of catalysts in hydrocarbon solutions were investigated in Refs.3, 5, 20-24, 43, 53-64 (Fig.12, Tables 4,5), where salt molecules were found to associate into micellas. About the dependence of oxidation rate on the concentration of the catalyst, opinions diverge. Just as with the oxidation of hydrocarbons in the gas phase in the presence of catalysts (Ref.65), also in the liquid phase in the presence of catalysts of variable valence the reaction course was observed to take place in successive macroscopic stages limited in time. (Refs.8, 7, 10, 59, 65, 55; Figs.13, 14). The causes of such a stepwise course could, up to now, only be explained in rough outlines. The study of the regulating action of the catalyst during oxidation is dealt with in Refs.10-12, 17, 21, 67-73 (Figs.15-20, Table 6). On the basis of existing experimental materials, the following may be stated on the

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Catalysis With Metals of Variable Valence in S/074/60/029/012/003/004
Oxidation Reactions in the Liquid Phase B013/B078

catalytic effect of metal salts of variable valence: The effect of salt catalysts upon oxidation is complicated and has various aspects. The catalysts react with oxidation products such as hydroperoxides and aldehydes under formation of free radicals. At the same time, several catalysts react with free radicals under tearing of chains. Under certain conditions, such catalysts have an inhibiting action upon oxidation. Besides, salt catalysts contribute to the lengthening of chains and regulate the composition of the resulting oxidation products. While the catalysts have an effect on the process of oxidation, they undergo complicated physicochemical transformations in their turn. Products of the developing reaction, particularly acids, extract the catalyst in the precipitate, which causes the further course of reaction to take place under a weaker participation of the catalyst. In spite of the complicated mechanism of catalytic oxidation, a number of symptoms could be determined, the knowledge of which will undoubtedly help in working out rigorously controllable oxidation methods. Mention is made of V. K. Tsyskovskiy, N. A. Kiseleva, and B. G. Freydin. There are 20 figures, 6 tables, and 73 references: 31 Soviet. ✓

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical
Physics of the AS USSR)
Card 3/3

5(4) 5.3200(A)

68616

AUTHOR: Denisov, Ye.T.

S/020/60/130/05/028/061

B004/B014

TITLE: A New Reaction for Initiating Chains in Liquid-phase Oxidation

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol 130, Nr 5, pp 1055-1058 (USSR)

ABSTRACT: The author presents an estimate of the rate W_0 of the initiation of chain reactions according to the equation $RH + O_2 \rightarrow R^* + HO_2^* - q_1$ (1). Table 1 lists experimental values of W_0 (ml/l.sec) and E_0 (kcal/ml) for benzaldehyde, decanal, cyclohexane, n-decane, Tetralin, and cyclohexanol. Calculation yields values which are too low and deviate from the experimental values by 5-10 orders of magnitude. As the values of E and of the steric factor f_1 assumed for calculation cannot lead to such great deviations, the author investigates the trimolecular reaction $RH + O_2 + HR \rightarrow R^* + H_2O_2 + R^* - q_2$ (2). The values calculated for W_0 according to equation (2) are compared in table 2 with those following from equation (1) and experimental values which are partly quoted from publications (Refs 2-6).

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A New Reaction for Initiating Chains in
Liquid-phase Oxidation

68616

S/020/60/130/05/028/061
B004/B014

The differences between W from equation (2) and experimental values amount to 1-2 orders of magnitude only. In consideration of the unavoidable errors of such an estimate, the author notes that the trimolecular reaction $2RH + O_2$ proposed by him is in satisfactory agreement with experimental data. Furthermore, this reaction forms the principal source of free radicals at the beginning of liquid-phase oxidation. This applies particularly to substances with easily separable C-H bonds (aldehydes, 1,4-diene hydrocarbons, and 1,3-diphenyl alkanes). There are 2 tables and 9 references, 4 of which are Soviet. ✓

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics of the Academy of Sciences, USSR)

PRESENTED: October 9, 1959, by V.N. Kondrat'yev, Academician

SUBMITTED: October 2, 1959

Card 2/2

11.5000
5.3200

S/020/60/132/03/29/066
B011/B008

AUTHORS: Denisov, Ye. T., Kharitonov, V. V.

TITLE: ¹Oxidation of Cyclohexanol¹ by Ozonized Oxygen

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 3,
pp. 595-597

TEXT: The authors oxidized 25-30 ml cyclohexanol by means of bubbling with oxygen which contained $0.3 \pm 0.03\%$ ozone, at a volume rate of 6.7 ± 0.7 l/h at 50-100°C. Cyclohexanone, H_2O_2 , adipinic acid and several esters develop by oxidation. The aggregation kinetics of the cyclohexanone and the H_2O_2 is at first linear, at a considerable intensity of the oxidation ($\sim 10\%$) the concentrations of the ketone and H_2O_2 pass a maximum. Data concerning the composition of the products after an oxidation lasting 2 hours are mentioned in Table 1. Compared with the thermal oxidation at 120°C, the products of the ozonized oxidation contain large amounts of acids and esters (10-20% instead of 1-2%). It follows from Table 1 that oxygen does not participate in the oxidation

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Oxidation of Cyclohexanol by Ozonized
Oxygen

S/020/60/132/03/29/066
B011/B008

at 50°C, but undoubtedly at higher temperatures. The authors presumed that all 3 oxygen atoms from the absorbed ozone are absorbed into the oxidation products. The authors further used hydroquinone as an inhibitor in order to check the chain mechanism of the reaction. It follows from Fig. 1 that a chain mechanism is here actually present. The problem whether the entire cyclohexanol or only part of it is oxidized in this way, remained unsolved. The authors found the answer thereto in their previous paper on the thermal oxidation of the cyclohexanol. Accordingly, the inclusion of the oxygen into the oxidation and the slowing down of the reaction by the inhibitor indicates that the reaction mechanism is chain-like. The assumption, however, that the reaction takes its course only chain-like, contradicts the data of the thermal oxidation of the cyclohexanol. There remains the only assumption that 2 oxidation mechanisms are present here: a chain mechanism with a rate v_{c} and a non chain-like with a rate v_{nc} . $v_{\text{c}} \approx v_{\text{nc}}$ equals the entering rate of the O_3 into the reaction vessel. $v_{\text{c}} \approx v_{\text{nc}}$ at lower temperatures, v_{c} increases with the temperature rise

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Oxidation of Cyclohexanol by Ozonized
Oxygen

S/020/60/132/03/29/066
B011/B008

(Table 2). From the energies of activation the authors come to the conclusion that the initiation of the chains by the decomposition of the ozone into O and O₂ does not play any significant role. The authors determined that the concentration of the cyclohexanone decreases at the introduction of the inhibitor at 100°C. This indicates a non chain-like reaction mechanism of the ozone with cyclohexanone (at the thermal oxidation cyclohexanone is only consumed on the chain way). A special experiment showed that the ozonized O₂ leads at 80°C and with an inhibitor to a non chain-like oxidation of the cyclohexanone. Acids are developed thereby (the inhibitor does not hamper the reaction). A possible scheme on the basis of the reaction of the ozone with the enol form of the ketone is mentioned. The authors conclude from the data that ozone reacts 20 times more quickly with cyclohexanone than with cyclohexanol. The authors thank V. G. Voronkov for his assistance with the experiments. N. M. Emanuel' is mentioned. There are 1 figure, 2 tables, and 3 Soviet references. 4

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR
(Institute of Chemical Physics of the Academy of Sciences
USSR)

Card 3/4

Oxidation of Cyclohexanol by Ozonized
Oxygen

S/020/60/132/03/29/066
B011/B008

PRESENTED: January 28, 1960, by V. N. Kondrat'yev, Academician

SUBMITTED: January 22, 1960

Card 4/4

23588
S/062/61/000/005/003/009
B118/B208

11.6200

AUTHOR: Denisov, Ye. T.

TITLE: The probability of self-inhibition of complicated chain reactions

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 5, 1961, 796 - 803

TEXT: A self-inhibition of complicated chain reactions, as in the oxidation of hydrocarbons, is a frequent phenomenon. It was studied for the first time by N. M. Emanuel' (Ref. 1: SM "Voprosy khimicheskoy kinetiki, kataliza i reaktsionnoy spetsobnosti" (Problems of Chemical Kinetics, Catalysis and Reactivity) Izd. ANSSSR, M., 1955, p 117). One of the causes of the self-inhibition of this reaction may be the change of the composition of the radicals during the reaction. The present paper deals with the probability of a self-inhibition of complicated chain reactions due to a change of the composition of the radicals. It is confirmed that this probability is very high. The composition of the radicals in a complicated chain reaction changes because the resulting intermediates react with the free radicals and give rise to the formation of radicals of

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B118/B208

The probability of...

another type. The complicated composition of the radicals occurring during the reaction affects the reaction rate. The author derives a formula expressing the change of the rate of consumption of the initial product as a result of the change of the radical composition: $F = \sum \alpha_{i0} n_i' / \sum \beta_i n_i'$.

α_{i0} equals k_{i0}/k_{00} , where k_{i0} denotes the constant of the reaction rate of the i-th radical; $n_i' = n_i/n$; n_i = concentration of the i-th radical;

n = total concentration of the free radicals; $\beta_i = k_i'/k_0$. With a very

high probability the complication of the radical composition during the reaction causes a self-inhibition of the complicated chain reaction. These calculations explain the cases of self-inhibition of oxidations and crack reaction, which frequently occur in experiments, and indicate the change of the radical composition to be a fundamental cause of this fact. Apart from the immediate effect on the rate of the chain reaction, the radical composition may also exert an indirect effect on this rate, i. e., by the concentration of the intermediate warranting the anomalous branching of the chains. This problem was discussed in the author's paper (Ref. 10: Izv. AN SSSR, Otd. khim. n. 1959, 2100), where it is confirmed that the

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The probability of...

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reduction of the function F which shows the change of the reaction rate only as a result of the changed radical composition, usually reduces the kinetic equilibrium concentration of the intermediate and, in addition, the reaction rate. The effect of the composition of the radicals on the intermediate concentration increases the probability of a self-inhibition of the anomalously branched chain reactions, contrary to the unbranched chain reactions. There are 5 figures and 10 Soviet-bloc references.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics of the Academy of Sciences USSR)

SUBMITTED: April 2, 1960

Card 3/3

S/076/61/035/002/014/015
B107/B220

AUTHORS: Denisov, Ye. T. and Kharitonov, V. V. (Moscow)

TITLE: Oxidation mechanism of cyclohexanol in liquid phase

PERIODICAL: Zhurnal fizicheskoy khimii, v. 35, no. 2, 1961, 444-451

TEXT: The aim of the study is to clear up the oxidation mechanism of secondary alcohols; the oxidation of pure cyclohexanol at 110, 120, and 130°C and at atmospheric pressure has been chosen as an example. 6 l of oxygen per hr were passed through a layer of 70 ml cyclohexanol. The reaction products were mainly peroxides (H_2O_2 and oxyalkyl hydroperoxide), cyclohexanone, water, and at the beginning of the reaction, also higher esters and acids. The peroxides were determined iodometrically, and the ketones with the help of hydroxylamine; the acids were titrated against phenolphthalein; the esters were determined by saponification with alcoholic soda lye. Moreover, the peroxides were determined again potentiometrically. The curve for the increase of cyclohexanone (Fig. 1) shows that the reaction proceeds autocatalytically; the curve for peroxide (Fig. 2) indicates that peroxide is an intermediate product of the reaction. α -naphthol was added as inhibitor

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Oxidation mechanism of ...

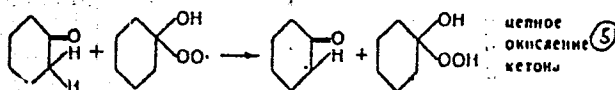
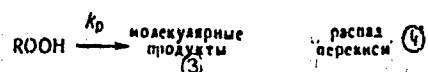
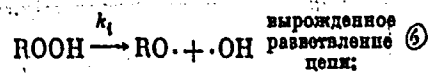
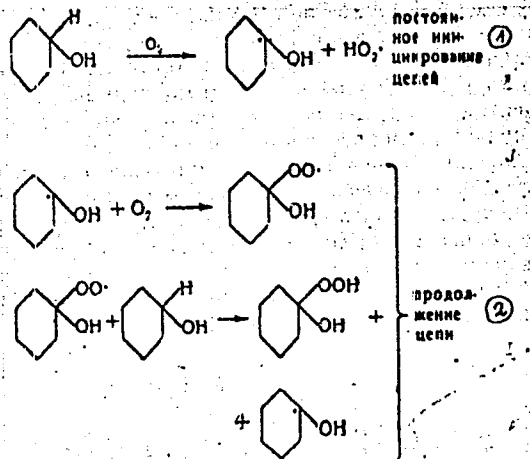
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B107/B220

to study the kinetics of reaction. The curves for cyclohexanol (Fig. 3) show that the reaction proceeds according to the chain mechanism only; this is different with peroxide: It can be seen from Fig. 4 that it is decomposed during oxidation without free radicals being involved. Furthermore, the rate of chain initiation was investigated (Fig. 5): At 120°C it increases from $0.27 \cdot 10^{-7}$ mole/l.sec to 10^{-6} mole/l.sec. The oxidation of cyclohexanol is, thus, a degenerate branching chain reaction; its autocatalysis is caused by the formation of peroxide and further chain-initiating products (Fig. 5). At 120°C the rate constant for the decomposition of the peroxide into free radicals is $1.34 \cdot 10^{-6}$ sec⁻¹. The chain length is reduced from 1000 at the beginning of the reaction to about 100 (Fig. 6). The activation energy of the chain lengthening amounts to 7.7 kcal/mole. The relative reactivity of cyclohexanol (k_1) and cyclohexanone (k_2) with peroxide radicals amounts to $k_2/k_1 = 2.1-2$ between 120 and 130°C. The oxidation mechanism of cyclohexanol is shown in the two schemes

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B107/B220



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Oxidation mechanism of ...

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B107/B220

There are 6 figures, 4 tables, and 8 references: 6 Soviet-bloc. The references to English language publications read as follows: Patent Brit. 708339 5-V-1954 (according to Chemical Abstracts 48, 11017, 1954); N. Brown, J. Amer. Chem. Soc., 77, 1765, 1955.

ASSOCIATION: Akademiya nauk SSSR Institut khimicheskoy fiziki (Academy of Sciences USSR, Institute of Chemical Physics)

SUBMITTED: June 26, 1959

Legend to Fig. 1: Kinetic curves showing the increasing content in cyclohexanone for the oxidation of cyclohexanol (1) at 110°C, (2) at 120°C, (3) at 130°C. (x) t in hr, (y) c in moles/l.

Legend to Fig. 2: Kinetics showing the increasing content in peroxide for the oxidation of cyclohexanol (1) at 110°C, (2) at 120°C, (3) at 130°C. (x) t in hr, (y) c in moles/l.

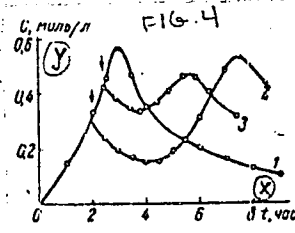
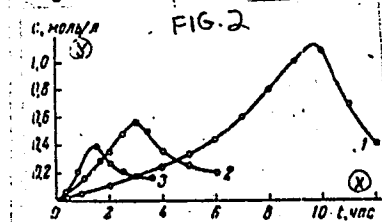
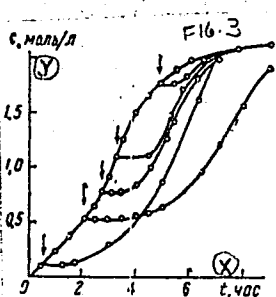
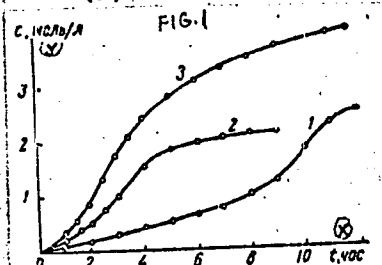
Legend to Fig. 3: Kinetics of ketone formation with α -naphthol as inhibitor at 120°C. The arrows indicate the instant at which the inhibitor was added. (x) t in hr, (y) c in moles/l.

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S/076/61/035/002/014/015
3107/3220

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Legend to Fig. 4: Kinetics of peroxide formation (1) in ordinary test, (2) and (3) with α -naphthol as inhibitor. (x) t in hr, (y) c in moles/l.



Card 5/6

DENISOV, Ye.T. (Moskva)

Various models of degenerated branching chain reactions with
one intermediate. Zhur.fiz.khim. 35 no.9:1966-1974 '61. (MIRA 14:10)

1. Akademiya nauk SSSR, Institut khimicheskoy fiziki.
(Chemical reaction, Rate of)
(Radicals (Chemistry))

30032
S/O20/61/141/001/017/02
B140/B101

54360

AUTHOR: Denisov, Ye. T.

TITLE: Chain formation mechanism during cyclohexanol oxidation

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 141, no. 1, 1961, 131 - 134

TEXT: It was experimentally found that the formation of free radicals during $C_6H_{11}OH$ oxidation in liquid phase was not $RH + O_2 \rightarrow R^\cdot + HO_2^\cdot$ (1) as had been assumed but $RH + O_2 + RH \rightarrow 2R^\cdot + H_2O_2$ (2). The experiments were conducted in a quartz vessel with reflux condenser. The vessel was heated and filled with 20 ml of $C_6H_{11}OH$ containing an α -naphthol ($10^{-3} - 1.5 \cdot 10^{-4}$ moles/liter) solution. The vessel was heated for another 5 min. and then an O_2 flow of 0.2 ml/sec was let in. α -naphthol was used as inhibitor: $InH + RO_2^\cdot \rightarrow In^\cdot + ROOH$; $In^\cdot + RO_2^\cdot \rightarrow InOOR$. Thus, its rate of consumption corresponded to the formation rate of free radicals: $W_o = 2(-d [InH]/dt)$. Samples were taken during the process, and their

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Chain formation mechanism during ...

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α -naphthol content was studied: Parasulfophenyl diazonium sulfate in methyl alcohol containing low amounts of alcoholic alkali was added to the sample. The dye thus forming was determined colorimetrically using a green filter. The accuracy of inhibitor concentration determination was $\pm 0.7\%$. At 121°C , the inhibitor only reacted with free radicals. During the first 100 min, the rate of inhibitor consumption was constant; then, it increased as the peroxide content increased. From the inclination of the kinetic curve for α -naphthol consumption, the formation rate of free radicals was calculated to be $8.3 \cdot 10^{-9}$ moles/liter \cdot sec. (A) The author studied the dependence of W_0 on the O_2 concentration at 111°C , an α -naphthol concentration of $2.5 \cdot 10^{-4}$ moles/liter, and at a pressure of 1 atm. The partial pressure of O_2 was changed by adding nitrogen. A linear increase of W_0 was observed: $W_c = W'_0 - aP_{O_2}$. (Fig. 2)

Without oxygen, $W_0 \neq 0$. Hence, the formation of free radicals was assumed to be due to the reaction of impurities without O_2 participation. The use of a pyrex glass vessel did not change the formation rate of free

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Chain formation mechanism during ...

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B140/B101

radicals. (B) The dependence of W_o on the $C_6H_{11}OH$ concentration was studied at $121^{\circ}C$ and an α -naphthol concentration of $1.5 \cdot 10^{-4}$ moles/liter. When dissolving $C_6H_{11}OH$ in chloro benzene, reduction of the $C_6H_{11}OH$ concentration caused a decrease of W_o . With pure C_6H_5Cl , $W_o = 0$. The curve shows that $W_o \sim [RH]$ and $W_o^{O_2} \sim [RH]^2$ with $W_o^{O_2}$ being the formation rate of the radicals during the reaction of $C_6H_{11}OH$ with O_2 . For $[RH]$ between 9.6 and 5.8 moles/liter, $\Delta \log W_o^{O_2} / \Delta \log [RH] = 2.3 \pm 0.2$. $W_o^{O_2} = k[RH]^n P_{O_2}$;

$\Delta \log W_o^{O_2} = n \Delta \log [RH] + \Delta \log P_{O_2}$. Hence,

$$n = \frac{\Delta \log W_o^{O_2}}{\Delta \log [RH]} - \frac{\Delta \log P_{O_2}}{\Delta \log [RH]} = 2.3 - \frac{\Delta \log P_{O_2}}{\Delta \log [RH]}. \quad P_{O_2} \text{ was } 393 \text{ mm Hg in } \checkmark$$

50 % mixture of $C_6H_{11}OH$ and C_6H_5Cl at $120^{\circ}C$. Hence,

$$\Delta \log P_{O_2} / \Delta \log [RH] = 0.15/0.30 = 0.5; n = 2.3 - 0.5 = 1.8 \pm 0.3, \text{ i. e. ,}$$

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Chain formation mechanism during ...

n practically equals 2. Hence, Eq. (2) proved to be correct. P_{O_2} was 630 mm Hg at 111°C, 1 atm, an O_2 concentration of $7.9 \cdot 10^{-3}$ moles/liter, and a $C_6H_{11}OH$ concentration of 9.6 moles/liter. Hence, the constant of the reaction rate: $k = 0.7 \cdot 10^{-8}$ liter²/mole²·sec. For reaction Eq. (2) an activation energy of 12 kcal/mole was obtained by studies in various temperature ranges. The real activation energy is somewhat higher due to O_2 concentration reduction in the liquid phase caused by a temperature elevation, a pressure increase of $C_6H_{11}OH$, and a P_{O_2} reduction. At 130°C, the real activation energy is 16 kcal/mole, and

$k = 8.3 \cdot \exp(-16000/RT)$ liter²/mole²·sec. There are 2 figures, 1 table, and 4 references: 3 Soviet and 1 non-Soviet. The reference to the English-language publication reads as follows: C. E. Boozer, G. S. Hammond, C. E. Hamilton, J. N. Sen, J. Am. Chem. Soc., 77, 5253(1955).

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics of the Academy of Sciences USSR)

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